

## Electrical Properties and Defect Structure of Rutile Slightly Doped with Cr and Ta

EIJI TANI\* AND JEAN FRANÇOIS BAUMARD†

*Centre de Recherches sur la Physique des Hautes Températures, CNRS 45045  
Orléans Cedex, France*

Received February 14, 1979

The electrical conductivity of rutile doped with 0.3–3 at % Ta or 0.1–1 at % Cr is reported as a function of oxygen pressure in the temperature range 1273–1623 K. The results are discussed in terms of a point defect model, on assuming a charge compensation of foreign impurities by usual lattice point defects. In the case of Ta-doped materials, two kinds of charge compensation by an electronic or a lattice defect may occur, according to the oxygen pressure and temperature, the essential features of which are in good agreement with the theoretical analysis. While chromium is incorporated as a trivalent species under a reducing atmosphere, the lack of ionic conductivity due to compensating lattice defects prevents any definitive conclusion about the valence state of the foreign chromium cations under oxidizing conditions. Some additional information and some conclusions are drawn concerning the transport properties of pure or doped titanium dioxide at high temperature.

### Introduction

Titanium dioxide,  $\text{TiO}_2$  rutile, has been the subject of several recent investigations at high temperature to elucidate the nature of defects responsible for the departure from stoichiometry when this oxide is treated under reducing conditions (1, 2). These investigations have shown that the range of existence of point defects, in the vicinity of 1273 K, extends from  $\text{TiO}_2$  to about  $\text{TiO}_{1.992}$ . Beyond that composition, it appears that a transition takes place, and the departure from stoichiometry is then accommodated by a crystallographic shear (CS) mechanism. A regular CS operation generates families of titanium suboxides, the structural aspects of which have been described in detail by several authors (3, 4).

\*Permanent address: Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.

†To whom correspondence should be addressed.

Another way to alter the oxygen/metal ratio is to introduce altermultivalent cations. Thus dopings with trivalent species as Cr, Fe, Ga have been the subject of structural investigations with the aid of X rays and electron microscopy. It has been shown that a suitable doping with Ga (5) leads to a complex series of intergrown phases, while introduction of Fe (6) or Cr (7–9) may lead to CS phases. As reported in an electron microscope study of the Fe–Ti–O system (6), the rutile field is probably quite small, say 0.1 to 1 at %, even at high temperature, and the obvious possibility of a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  transition under reducing conditions makes a thermodynamic approach difficult. On the other hand, it has been reported in several papers (3, 6, 7) that rutile and chromia exist as a solid solution, in the range 0 up to about 5 mole%  $\text{CrO}_{1.5}$ , before the appearance of  $\text{Cr}_2\text{Ti}_{n-2}\text{O}_{2n-1}$  compounds, below 1730 K. The reason why the rutile lattice is able to assimilate such a content of chromia is still unknown. Flörke

and Lee (5) argued that chromium enters the empty octahedral sites, forming two-dimensional defects coherent with the mother structure. They also suggested that chromium may well be incorporated as  $\text{Cr}^{4+}$  to build up a perfect rutile lattice. But there is no microscopic evidence for a clustering of  $\text{Cr}^{3+}$  into interstitial disks (3), and a lot of spectroscopic data mainly due to ESR support the idea that chromium substitutes normal titanium lattice sites as  $\text{Cr}^{3+}$  (10-12). The charge compensation would then be ensured by a subsequent classical anion deficiency. The semiconducting properties are generally affected by a small content of impurities, and they are sensitive both to their location and valence states in the host matrix. Thus some attention has been paid recently to the electrical conductivity of Cr-doped  $\text{TiO}_2$  (13), but the restricted range of oxygen pressure was much too small to draw any definitive conclusion. A detailed analysis of the influence of trivalent cations has not been performed.

In the same way, incorporation of a  $\text{Me}^{5+}$  pentavalent species, as  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$ , increases the anion/cation ratio and normally leads to an overstoichiometric oxide  $\text{Ti}_{1-y}\text{Me}_y^{5+}\text{O}_{2+y/2}$ . Rutile is indeed reported to accept a few mole% of  $\text{NbO}_{2.5}$  (14, 15) or  $\text{TaO}_{2.5}$  (16) in solid solution. Both electron microscopy and neutron diffraction experiments, reported by Anderson (3), failed to reveal a possible hyperstoichiometric shear or clustering in these materials. A previous study (15) has shown that the semiconducting properties of Nb-doped rutile may be understood in terms of a point defect model, under the assumption of a substitutional incorporation of niobium, that is largely sustained by ESR results (17). It is expected that, owing to the stability of the  $\text{Ta}^{5+}$  ion, demonstrated for instance by transport properties (18) and ESR experiments (19) of a Ta-doped rutile at low temperatures, similar results should be obtained for this material.

These are the reasons why following the previous papers dealing with pure rutile (1), and Nb-doped rutile (15) it was attempted to get additional results about the defect structure and related properties from the semiconducting behavior of Cr- or Ta-doped oxides, that is depicted below.

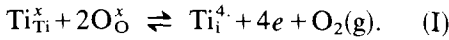
## Experimental

Polycrystalline specimens with a variable composition were prepared by intimate mixing of known quantities of titanium dioxide (Johnson Matthey Specpure) and tantalum oxide or chromium carbonate (reagent grade materials). The powder was then pressed into rods. The chromium-doped oxides were sintered at a moderate temperature to avoid evaporation of chromia, e.g., for 24 hr at 1670 K, followed by 6 hr at 1720 K. Tantalum-doped rutile was first melted in a plasma jet, then ground in an agate mortar, pressed, and finally sintered at 1670 K for several hours in air and under reducing conditions. This procedure ensured a uniform distribution of tantalum inside the sample. The specimens were shaped into cylinders, about 25 mm long and 4 mm in diameter, with the aid of diamond tools, then coated with Pt wire and Pt paste for the measurement of electrical conductivity in a standard 4 probe dc method. The other experimental conditions have been described previously (1). The range of oxygen partial pressure that has been swept in the present case of doped oxides is the same as in our previous study of point defects in pure  $\text{TiO}_{2-x}$  (1).

## Theory

The purpose here is to examine the effect of altrivalent cations upon the concentration of the defect species, according to the general rules of controlled valency (20), with the aid of a point defect model. It will be assumed that the doping  $\text{M}^{3+}$  or  $\text{Me}^{5+}$  cations substi-

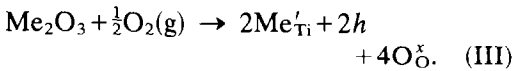
tute titaniums on normal lattice sites. The compensation of the deficit or excess charge may be ensured by an electronic or a lattice defect, according to the temperature and the oxygen partial pressure. In pure rutile, there is recent experimental evidence from the semiconducting properties (1, 21, 22) that, for compositions close to TiO<sub>2</sub>, titanium interstitials are responsible for the departure from stoichiometry in the temperature range of this study, beyond 1250 K, according to



The Kröger Vink notation will be used throughout this paper. It will then be assumed that the lattice defect involved in the charge compensation of a substitutional trivalent impurity is a titanium interstitial,



while under a high oxygen pressure a charge compensation by an electron hole is a priori possible, according to



To get the concentration of the different point defect species, one has to write down the local charge balance,

$$4[\text{Ti}_i^{4+}] + p = n + [\text{M}'_{\text{Ti}}], \quad (\text{1})$$

where  $n$  and  $p$  are the electron and electron hole concentrations, while  $[ ]$  denote the concentrations of the lattice defects considered. Following the quasi-chemical approach of the point defect model, the mass action law may be applied to equilibrium (I)

$$K_1 = [\text{Ti}_i^{4+}]n^4 p_{\text{O}_2}, \quad (\text{2})$$

where  $p_{\text{O}_2}$  denotes the oxygen partial pressure, and one has to take the thermal excitation across the band gap into account:

$$K_i = np. \quad (\text{3})$$

According to the temperature and the oxygen pressure, Eq. (1) simplifies and the situation is depicted schematically in Fig. 1a, where three ranges A, B, and C occur corresponding to  $(\text{M}, \text{Ti})\text{O}_{2-x}$ ,  $\text{M}_y^{3+}\text{Ti}_{1-y}^{4+}\text{O}_{2-y/2}$ , and  $\text{M}_y^{4+}\text{Ti}_{1-y}^{4+}\text{O}_2$  respectively. In range A, a  $-\frac{1}{5}$  logarithmic dependence for  $\log n$  versus  $\log p_{\text{O}_2}$  is found, similar to that of pure rutile, when the content of native defects prevails over the dope effect. In range B, on the other hand, the titanium interstitial concentration depends upon the  $\text{M}^{3+}$  content, and a characteristic  $-\frac{1}{4}$  dependence should be observed between  $\log n$  and  $\log p_{\text{O}_2}$ :

$$n = (4K_1)^{1/4}[\text{M}'_{\text{Ti}}]^{-1/4}p_{\text{O}_2}^{-1/4}. \quad (\text{4})$$

One also notices that a high ionic transference number can then be reasonably

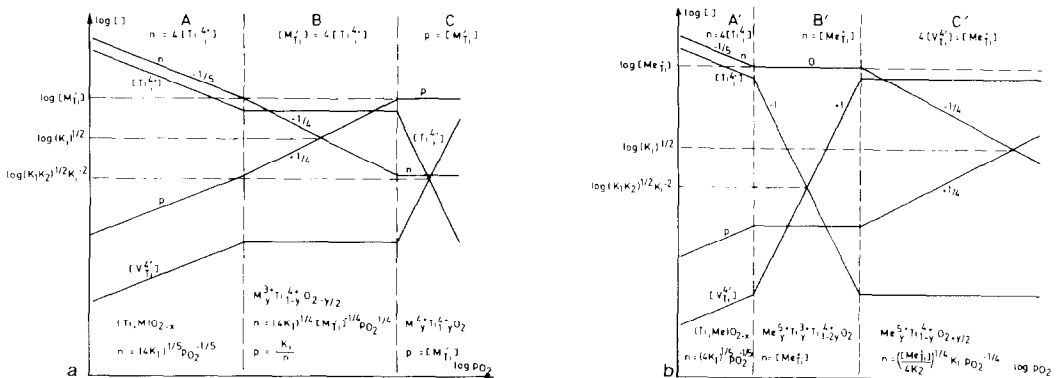
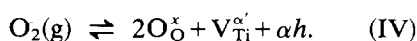


FIG. 1. The variation of the defect concentrations versus oxygen partial pressure for  $\text{M}^{3+}$  (a) or  $\text{Me}^{5+}$  (b) doped rutile, under the assumptions:  $[\text{M}'_{\text{Ti}}], [\text{Me}'_{\text{Ti}}] \gg K_i^{1/2} \gg (K_1 K_2)^{1/2} K_i^{-2}$  and  $\alpha = 4$ .

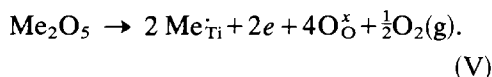
expected, because the concentration of mobile titanium interstitials becomes much greater than the concentration of electronic defects. The general equation describing the variation of  $n$  as a function of  $p_{O_2}$  is given by Eqs. (1) to (3):

$$4K_1n^{-4}p_{O_2}^{-1} + K_2n^{-1} = n + [M'_{Ti}]. \quad (5)$$

Turning now to the case of incorporation of a  $Me_2O_5$  oxide, it will be there assumed that the lattice defect involved in the charge compensation is a titanium vacancy  $V_{Ti}^{\alpha'}$ , where  $\alpha$  denotes the ionization state of the vacancy. In fact, the present experiment is unable to elucidate whether the compensation is operated by a titanium vacancy or an oxygen interstitial, but in absence of extended defects, a compensation by oxygen interstitials seems to be less reliable, owing to the close packed character of the oxygen sublattice in rutile. The defect analysis is thus restricted to the case of a titanium vacancy, but similar conclusions could be reached in the case of an oxygen interstitial mechanism:



Under moderately reducing conditions, the extra charge of a pentavalent cation is expected to be compensated by an electron, according to



In that range the electron carrier concentration will depend linearly on the dope content, for the small  $Me/Ti$  ratios of interest here. The quasi-chemical treatment is now applied to equilibrium (IV),

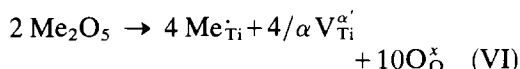
$$K_2 = [V_{Ti}^{\alpha'}]p^\alpha p_{O_2}^{-1}, \quad (6)$$

while the charge balance implies

$$[Me_{Ti}^{\cdot}] + 4[Ti_i^{4\cdot}] + p = n + \alpha[V_{Ti}^{\alpha'}]. \quad (7)$$

According to the temperature and the oxygen pressure, Eq. (7) simplifies and a tenta-

tive concentration diagram is depicted on Fig. 1b, with  $\alpha = 4$ , under some assumptions that will be discussed later on. Again three ranges A', B', and C' occur. The behaviour in range A' is similar to that of pure rutile, for the same reasons as in the case of trivalent impurities. In range B', corresponding to a "MeO<sub>2</sub>-TiO<sub>2</sub>" solid solution, the electron carrier concentration is not dependent on  $p_{O_2}$ , but is simply related to the Me content. The atomic defect concentration then varies promptly with  $p_{O_2}$ , and this leads to an over-stoichiometric oxide in range C', where



and

$$n = [Me_{Ti}^{\cdot}]^{1/\alpha} (\alpha K_2)^{-1/\alpha} K_1 p_2^{-1/\alpha}. \quad (8)$$

A linear logarithmic dependence with a  $-1/\alpha$  slope between  $n$  and  $p_{O_2}$  should be observed with a  $1/\alpha$  relationship between  $\log n$  and  $\log [Me_{Ti}^{\cdot}]$ . As far as the electron hole and ionic contribution are negligible, the electrical conductivity should follow the same laws. These features have indeed been observed in the case of Nb-doped TiO<sub>2</sub>. This semiconductor remains largely  $n$  type and in range C' the Fermi level lies in the upper part of the band gap. Then the high energy levels of titanium vacancies are occupied by electrons from the Nb donors. On taking  $\alpha = 4$ , this leads to a  $-1/4$  slope for the conductivity isotherms.

Neglecting the electron hole contribution, as justified below, the general relationship between  $n$  and  $p_{O_2}$  follows from Eqs. (2), (6), and (7):

$$[Me_{Ti}^{\cdot}] + 4K_1n^{-4}p_{O_2}^{-1} = n + K_2K_1^{-\alpha}n^\alpha p_{O_2}. \quad (9)$$

It is noteworthy that a doping with  $Me^{5+}$  cations can give useful information about metal deficiency, that is not observed in pure rutile.

## Results and Discussion

### The Case of Chromium-Doped Rutile

The experimental data for chromium-doped rutile are plotted versus oxygen partial pressure in Figs. 2a and b, with Cr/Ti ratios extending from 0.1 to 1 at%. Two curves previously published (15) for an undoped polycrystalline specimen are also reported on the same figures for comparison. There is a change in the slope of the isotherms, from  $-\frac{1}{5}$  for pure rutile to  $-\frac{1}{4}$  for doped materials. Under quite a reducing atmosphere, there is a trend toward the behavior of the undoped rutile, as mentioned in the previous section, since the departure from stoichiometry is here induced by native defects rather than by chromium. A  $n$ - $p$  transition is also observed in the vicinity of 1 atm oxygen. A similar transition has already been reported by Yahia (23) and Rudolph (24) on Al- and Fe-doped  $\text{TiO}_2$ , respectively, but their experiment was limited to the high oxygen pressure side ( $10^{-5}$  to 1 atm). No quantitative treatment has been proposed by Rudolph, whereas the incorporation of Al is probably complex (25).

The electron carrier concentration may be calculated according to Eqs. (5) and (3), in which  $K_1$  is known from studies of both poly- and monocrystalline titanium dioxide (1,15), while  $K_i$  may be estimated from thermoelectric power data (26). The values that

were used are reported in Table I. All the chromium was assumed to enter the lattice as  $\text{Cr}'_{\text{Ti}}$  in a trivalent state. Then the electrical conductivity may be calculated according to:

$$\sigma = (n + p)q\mu \quad (10)$$

where the mobilities of electrons and holes were assumed to be equal, with  $\mu = 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  (15).

The theoretical curves are in good agreement with the experimental data at low oxygen pressures, and considering some probable error in the indirect estimation of  $K_i$ , they also show a fair agreement on the high oxygen pressure side. It is to be noted that the electronic conductivity does not always decrease with addition of chromia, mainly in the vicinity of 1 atm  $\text{O}_2$ , as reported by Anzai (13). It depends upon the respective contributions of electrons and electron holes at a given temperature. Thus a model taking the electronic conductivity only into account fits the experimental data satisfactorily for these Cr/Ti ratios. One can notice that under a low oxygen pressure, chromium is well incorporated as a  $3+$  species, with a charge compensation by a lattice defect. This is the only way to explain a  $-\frac{1}{4}$  slope.

Nevertheless, the theoretical ionic conductivity  $\sigma_{\text{Ti}}^{\text{th}}$  due to mobile titanium interstitials may also be calculated if they act as isolated point defects. On taking the classical expression of ionic conductivity derived

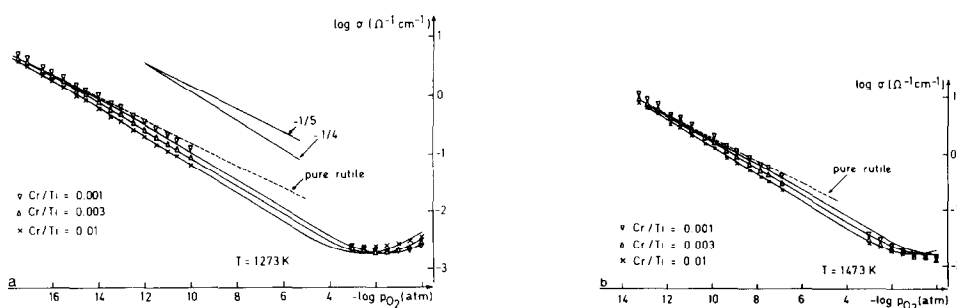


FIG. 2. (a, b) A plot of electrical conductivity of Cr-doped rutile versus oxygen pressure. Full lines have been calculated using Eqs. (3), (5), and (10).

TABLE I  
PARAMETERS THAT ENTER CALCULATIONS OR  
CURVE FITTING FOR Cr- OR Ta-DOPED RUTILE<sup>a</sup>

T (K)	1273	1473	1623
$K_1$	$2.4 \cdot 10^{84}$	$5.3 \cdot 10^{89}$	$7.5 \cdot 10^{92}$
$K_i$	$3.3 \cdot 10^{33}$	$2.6 \cdot 10^{35}$	—
$K_2 K_i^{-4}$	$5.9 \cdot 10^{-58}$	$1.6 \cdot 10^{-60}$	$2.6 \cdot 10^{-62}$

<sup>a</sup> Concentrations and oxygen pressure in  $\text{cm}^{-3}$  and atm units, respectively.

from the Nernst–Einstein relationship (27):

$$\sigma_{\text{Ti}}^{\text{th}} = C_{\text{Ti}} D_{\text{Ti}} (z_{\text{Ti}} q)^2 / kT,$$

where  $C_{\text{Ti}}$ ,  $D_{\text{Ti}}$ , and  $z_{\text{Ti}}$  refer to the concentration, the ionic diffusion coefficient, and the valence of titaniums, and on taking the relationship between  $D_{\text{Ti}}$  and the coefficient of chemical diffusivity of oxygen  $\tilde{D}$  (21):

$$\tilde{D} = 5 D_{\text{Ti}} / N_{\text{Ti}^{4+}}$$

where  $N_{\text{Ti}^{4+}}$  denotes the molar fraction of titanium interstitials, it turns out:

$$\sigma_{\text{Ti}}^{\text{th}} = [\text{Ti}_i^{4+}] \tilde{D} (z_{\text{Ti}} q)^2 / 5 kT.$$

In range B, where

$$4[\text{Ti}_i^{4+}] = [\text{Me}'_{\text{Ti}}],$$

it follows that

$$\sigma_{\text{Ti}}^{\text{th}} = [\text{Me}'_{\text{Ti}}] \tilde{D} (z_{\text{Ti}} q)^2 / 20 kT. \quad (11)$$

The coefficient of chemical diffusivity of oxygen has been measured previously (21) for the  $c$  axis of rutile single crystals. There is no evidence for a large difference between the  $c$  and  $a$  directions, as the titanium tracer diffusion coefficients are of a comparable order of magnitude for the two crystallographic directions (28). On taking a mean value of  $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$  for  $\tilde{D}$ , one gets from Eq. (11),

$$\sigma_{\text{Ti}}^{\text{th}} = 3 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1},$$

for  $\text{Cr}/\text{Ti} = 0.01$ . The experimental value of the conductivity is smaller by about one order of magnitude in the vicinity of 1 atm oxygen at 1273 K. As a consequence, we did

not attempt to measure the ionic transference number, that is certainly quite small. An absence of ionic contribution is furthermore indicated by the poor, if any, dependence of the minima of conductivity on the chromium content, and the lack of a flat portion in the isotherms. Thus either the compensating defects do not behave as isolated point defects, or chromium is also incorporated as a neutral species  $\text{Cr}_{\text{Ti}}^x$ .

The reason why this happens is not clear at the present time. One can first consider the suggestion of Flörke and Lee (7), about incorporation of chromium as  $\text{Cr}^{4+}$  on normal lattice sites. A  $\text{Cr}^{3+}/\text{Cr}^{4+}$  transition from a reducing to an oxidizing atmosphere should introduce a new equilibrium:



As the content of neutral  $\text{Cr}_{\text{Ti}}^x$  impurities increases with oxygen pressure, less mobile lattice defects are needed for the charge balance, and the ionic conductivity should be smaller than calculated before. But it is difficult to introduce a new significant parameter into Eq. (5), taking this equilibrium (VII) into account. Qualitatively, when the  $p$  type conductivity is significant, the Fermi level should drop considerably in the forbidden gap and could cross over a  $\text{Cr}^{3+}/\text{Cr}^{4+}$  level. The amount of ESR work about Cr-doped rutile supports an incorporation as  $\text{Cr}^{3+}$ , and it has even been reported that no increase of  $\text{Cr}^{3+}$  signal happens when the crystals are treated under a reducing atmosphere (12). However, the chromium content of interest in ESR is generally very small, well below 0.1 at% and a change in the valence state, in the doping range of this study, cannot be ruled out. Also the possibility remains that a clustering between impurities and lattice defects takes place, due to electrostatic interaction or lattice relaxation. This should imply a smaller mobility of compensating defects. It is not possible at the present stage to give a definitive explanation.

Finally it is noticeable that a small fraction of trivalent cations raises a  $n$ - $p$  transition for a nondeliberately doped rutile. This reinforces our previous interpretation of the semiconducting properties of nearly stoichiometric rutile  $\text{TiO}_{2-x}$  ( $x \leq 10^{-4}$ ), where trivalent impurities play a major role (1).

#### The Case of Tantalum-Doped rutile

The conductivity curves are reported as a function of oxygen pressure in Figs. 3a and b, for Ta/Ti ratios extending from 0.003 to 0.03. The features predicted in the previous section for a  $\text{Me}^{5+}$ -doped rutile are again well observed. At 1273 K, for instance, for Ta/Ti = 0.003, the  $-\frac{1}{5}$ , 0, and  $-\frac{1}{4}$  slopes of the plots are representative of reduced rutile  $(\text{Me}, \text{Ti})\text{O}_{2-x}$ , nearly stoichiometric  $\text{Ta}_y^{5+}\text{Ti}_y^{3+}\text{Ti}_{1-2y}^{4+}\text{O}_2$ , and overstoichiometric  $\text{Ta}_y^{5+}\text{Ti}_{1-y}^{4+}\text{O}_{2+y/2}$  solid solutions, respectively, corresponding to the three ranges A', B' and C' of Fig. 1b.

In range B', the electrical conductivity can be shown to be linearly dependent upon the introduced concentration of tantalum. Thus a complete exhaustion of Ta levels is achieved and the electron mobility, when assuming a free electron carrier per  $\text{Ti}^{3+}$  in  $\text{Ta}_y^{5+}\text{Ti}_y^{3+}\text{Ti}_{1-2y}^{4+}\text{O}_2$ , turns out to be equal to  $0.1 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ , in good agreement with other studies on pure or Nb-doped  $\text{TiO}_2$  (1, 15). In range C', the  $-\frac{1}{4}$  slope of the isotherms reveals a high ionization state for

the titanium vacancies  $\text{V}_{\text{Ti}}^{4'}$ . This is in fact somewhat expected, since the electron carrier concentration is high. The Fermi level lies in the vicinity of the conduction band and the highest energy levels are occupied by electrons from the Ta donors.

The electrical conductivity can now be calculated using Eqs. (9) and (10), where the small contribution of electron holes is neglected. In Eq. (9),  $[\text{Ta}_{\text{Ti}}^+]$  was assumed to be equal to the introduced Ta content, and the value of  $K_2 K_i^{-4}$  has been adjusted to fit the data at a given Ta/Ti ratio as mentioned in Figs. 3a and b. The agreement of calculated curves and experimental data is fairly good in ranges A' and B'. In range C', the agreement is good only for slightly doped specimens, containing less than 1 at% at 1273 K to 3 at% at 1623 K. At higher Ta contents, a  $-\frac{1}{4}$  slope is found for the  $\log \sigma$ - $\log p_{\text{O}_2}$  plots, but the electrical conductivity becomes relatively insensitive to the degree of doping, in disagreement with Eq. (8). This is in close similitude with the results obtained in the case of Nb-doped rutile (15). While the field of solid solutions of  $\text{TaO}_{2.5}$  or  $\text{NbO}_{2.5}$  in rutile is reported to extend to 4–8 at% (14, 16), the semiconducting properties behave as in a two phase system, where the maximum solubility would be reached, and the activity of tantalum or niobium would be fixed by precipitates of  $\text{TiTa}_2\text{O}_7$  or  $\text{TiNb}_2\text{O}_7$  in the matrix. This probably stems from

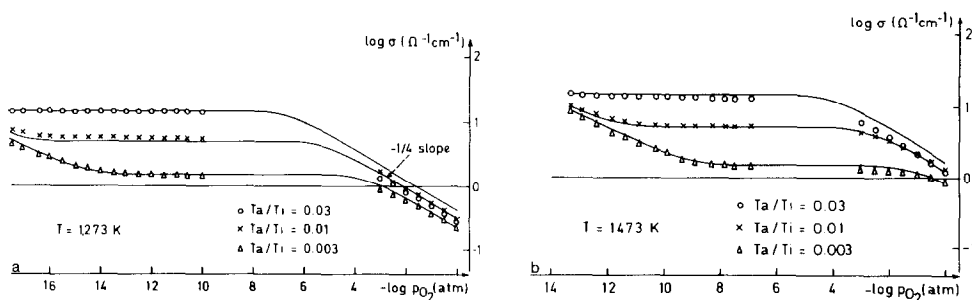
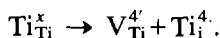


FIG. 3. (a, b) A plot of electrical conductivity of Ta-doped rutile versus oxygen pressure. The model predicted by Eq. (9) has been fitted on the high oxygen pressure side, for the composition Ta/Ti = 0.01 at 1273 and 1473 K.

defect associations due to differences in ion sizes for  $\text{Ti}^{4+}$  and  $\text{Ta}^{5+}$  or  $\text{Nb}^{5+}$ , or coulombic interactions between substitutional cations and highly charged titanium vacancies. However the hypothesis of noninteracting point defects is well verified, at least for a small degree of doping.

The variation of  $K_2K_i^{-4}$  has been plotted versus temperature in Fig. 4. The data fall on a straight line, with an activation energy of  $-4.8$  eV. On taking an activation energy of  $10.6$  eV for reaction (I), one finds that  $5.8$  eV are needed for the creation of a Frenkel pair, according to



Unfortunately, this value cannot be compared to any other one, since no oxide with the rutile structure, to our knowledge, presents this kind of disorder. It is also difficult at this stage to bring the theoretical calculations of Catlow *et al.* into comparison, since there is more experimental evidence in favour of titanium interstitials, whereas atomistic calculations support a Schottky disorder (29).

### Conclusions

Some conclusions concerning the defect structure and the transport properties can be

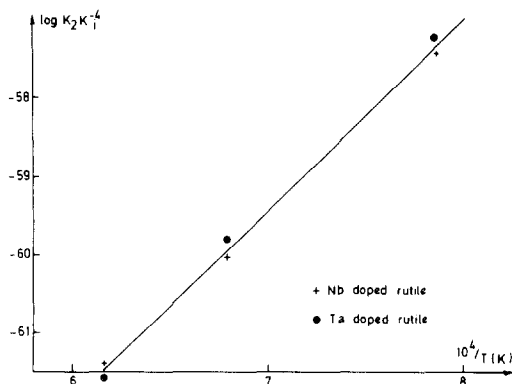


FIG. 4. The variation of  $K_2K_i^{-4}$  against temperature for Ta- and Nb-doped materials.

drawn from this study. First trivalent and pentavalent species that may be incorporated substitutionally in rutile deeply affect the semiconducting properties. For instance, a  $3+$  impurity brings about a change from a  $-\frac{1}{5}$  to a  $-\frac{1}{4}$  slope for the conductivity isotherms. At low concentrations of chromium or tantalum, the variation of electrical conductivity versus oxygen partial pressure or dope content is well understood in terms of a compensation by usual point defects. However when the content of altrivalent impurities increases, say beyond 1 at% at 1300 K, some clustering probably takes place, that is revealed by significant departures from the predicted ideal behavior of the electron carrier concentration when plotted versus dope content, in the case of Nb, Ta as well as Cr (30) doped rutiles. Unless purely thermodynamic activity effects that cannot be evaluated quantitatively at the present time could explain such significant departures, complex defects could arise, too small to be detected by lattice imaging, before the appearance of a next compound  $\text{TiMe}_2\text{O}_7$  ( $\text{Me} = \text{Ta}, \text{Nb}$ ), or a CS structure in the Ti-Cr-O system.

Turning now to the more specific case of Cr-doped  $\text{TiO}_2$ , a  $\text{Cr}^{3+}/\text{Cr}^{4+}$  transition under oxidizing conditions is not ruled out by the semiconducting properties, and it could even explain the lack of ionic conductivity. One may also conclude that a significant  $p$  type conductivity should not be obtained at room temperature. Doping with a  $3+$  impurity leads at high temperature to a compensated semiconductor, that becomes more or less insulating at room temperature.

Finally, as underlined in a previous paper (15), the calculated concentration of titanium vacancies  $\text{V}_{\text{Ti}}^{4'}$  is quite small for pure rutile, and the presence of trivalent impurities that are unavoidable still decreases this value well below the ppm level. Thus while the titanium self-diffusion experiments were generally interpreted by assuming a vacancy



mechanism, it appears more probable that this occurs via interstitials, the concentration of which is larger.

## References

1. J. F. BAUMARD, D. PANIS, AND A. M. ANTHONY, *J. Solid State Chem.* **20**, 43 (1977).
2. J. F. BAUMARD, D. PANIS, AND D. RUFFIER, *Rev. Int. Hautes Temp. Refract.* **12** 321 (1975).
3. C. PICARD AND P. GERDANIAN, *J. Solid State Chem.* **14**, 66 (1975).
4. J. S. ANDERSON, in "Surface and Defect Properties of Solids," Chap. 1, p. 1, Specialist Periodical Reports, The Chemical Society, London 1972.
5. L. A. BURSILL AND B. G. HYDE, *Progr. Solid State Chem.* **7**, 177 (1972).
6. G. G. STONE AND L. A. BURSILL, *Phil. Mag.* **35**, 1397 (1977).
7. L. A. BURSILL, D. J. NETHERWAY, AND I. E. GREY, *Nature (London)* **272**, 405 (1978).
8. L. A. BURSILL, I. E. GREY, AND D. J. LLOYD, *J. Solid State Chem.* **16**, 331 (1976).
9. O. W. FLORKE AND C. W. LEE, *J. Solid State Chem.* **1**, 445 (1970).
10. R. M. GIBB AND J. S. ANDERSON, *J. Solid State Chem.* **4**, 379 (1972).
11. S. SOMIYA, S. HIRANO, AND S. KAMIYA, *J. Solid State Chem.* **25**, 238 (1978).
12. H. J. GERRITSEN, J. E. HARRISON, AND H. R. LEWIS, *J. Appl. Phys.* **31**, 1566 (1960).
13. M. IKEBE, Y. MIYAKO, AND M. DATE, *J. Phys. Soc. Jpn.* **26**, 43 (1969).
14. D. N. MIRLIN, I. I. RESHINA, AND L. S. SOCHAVA, *Sov. Phys. Solid State* **11**, 1995 (1970).
15. K. ANZAI, S. HIRANO, AND S. SOMIYA, *Bull. Tokyo Ins. Technol.* **120**, 65 (1974).
16. N. G. EROR AND D. M. SMYTH, in "The Chemistry of Extended Defects in Non Metallic Solids," p. 62., North-Holland, Amsterdam, 1970.
17. J. F. BAUMARD AND E. TANI, *J. Chem. Phys.* **67**, 857 (1977).
18. W. MERTIN, R. GRUEHN, AND H. SCHAFFER, *J. Solid State Chem.* **1**, 425 (1970).
19. P. M. ZIMMERMANN, *Phys. Rev.* **B 8**, 3917 (1973).
20. O. MONNERAU AND A. CASALOT, *J. Solid State Chem.* **23**, 399 (1978).
21. P. F. CHESTER, *J. Appl. Phys.* **32**, 866 (1961).
22. For instance, see G. G. LIBOWITZ, in "Treatise on Solid State Chemistry" (N. B. HANNAY, Ed.), Vol. 1, p. 335, Plenum, New York 1975.
23. J. F. BAUMARD, *Solid State Commun.* **20**, 859 (1976).
24. R. N. BLUMENTHAL, J. BAUKUS, AND W. M. HIRTHE, *J. Phys. Chem. Solids* **27**, 643 (1966).
25. J. YAHIA, *Phys. Rev.* **130**, 1711 (1963).
26. J. RUDOLPH, *Z. Naturforsch. A* **14** 727 (1969).
27. D. SWINGEL, *Solid State Commun.* **20**, 397 (1976).
28. J. F. BAUMARD AND E. TANI, *Phys. Status Solidi A* **39**, 373 (1977).
29. P. KOFSTAD, in "Non Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides," p. 87, Wiley, New York, 1972.
30. T. S. LUNDY AND W. A. COGHLAN, *J. Phys. (Paris), Colloq.* **C 9**, 299 (1973).
31. C. R. A. CATLOW, R. JAMES, AND M. J. NORGETT, *J. Phys. (Paris), Colloq.* **C 7**, 443 (1976).
32. E. TANI AND J. F. BAUMARD, unpublished results.